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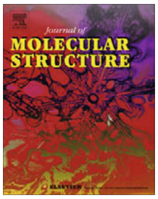

Infrared spectroscopy and *ab initio* computation in conformer determination of keto ester and diketo triphenylphosphonium ylides

Clifford A. Bunton [a], Fernando Castañeda [b,*]

[a] *Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106, USA*
[b] *Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile*

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ABSTRACT

For stabilized triphenylphosphonium keto ester ylides acyl stretching frequencies of the *anti* ester group from HF/6-31G(d) calculations fit experimental values with Scale Factor, SF = 0.866, as estimated earlier for the diester ylides, but Scale Factor = 0.834 has to be used to fit data for the *syn*-keto group and for *syn–anti* diketo ylides. The DFT functional BLYP/6-31G(d), with the literature Scale Factor = 0.9945, generally gives good fits for both keto ester and diketo ylides. For both methods agreement between observed and predicted frequencies is lowest for the *syn–anti* di-*t*-butyl keto ester ylide, although, unlike the situation for diester ylides, one bulky alkyl group does not significantly degrade the fits. Comparison of predicted and observed acyl stretching frequencies is useful in establishing conformations of these stabilized phosphonium ylides.

1. Introduction

Phosphonium ylides with a single keto or ester substituent can adopt two conformations [1–3] and *syn* and *anti* indicate orientations of the acyl group with respect to phosphorus. The *syn* conformer is generally energetically preferred over the *anti*, due to interactions between anionoid oxygen and cationoid phosphorus and in favorable cases interconversion is slow on the NMR time scale [4,5].

Ylides with two identical acyl groups can adopt three conformations and with different acyl groups four conformers could form, but in most of the stabilized ylides with alkyl acyl groups examined to date one conformer is dominant, usually with *syn–anti* acyl, but sometimes *anti–anti* groups, [6–11]. These generalizations only apply to ylides with alkyl keto or ester groups and Aitken et al. in considering ylides with phenyl or very bulky groups in the ylidic moiety observed a number of systems where two acyl groups adopted the *syn–syn* conformation [12]. There would be resonance between these phenyl groups and the ylidic moiety and such interactions and non-bonding interactions of very bulky groups should not be important in the alkyl ketones and esters that we examined. In the present work we examined triphenylphosphonium derivatives and designated conformations as *syn* or *anti* depending on orientations of the two acyl groups with respect to phosphorus (Scheme 1).

The classical structures in Scheme 1 are inadequate because there is free rotation about the P–C bond on the NMR time scale and considerable double bond character between the ylidic and acyl carbons. Classical structures can be written as zwitterionic [13] with a P–C single bond and positive charge on phosphorus and negative charge on the ylidic carbon but there should be extensive ylidic resonance with partial charges on these atoms. For alkyl diester ylides *syn–syn* conformers have not been detected, but both *syn–anti* and *anti–anti* conformers have been identified and in the *syn–anti* diester ylides the bulkier alkoxy group is preferentially oriented towards phosphorus in the crystal and in solution [9,11]. In the diesters only one conformer is usually observed, but the crystalline dimethyl diester, X = OMe, is a 1:1 mixture of *syn–anti* and *anti–anti* conformers [10,11], although only one set of ^{1}H or ^{13}C NMR signals are observed in solution, possibly because conformers interconvert rapidly on the NMR time scale. The use of Infrared, IR, spectroscopy does not have this limitation, but prediction of frequencies is a problem, and this method lacks the quantitative power of NMR spectroscopy.

Infrared spectra of phosphonium ylides are complicated [14], but stretching frequencies of acyl and cyano groups can usually be identified with limited overlap with other signals. For given structures IR frequencies can be estimated by using a variety of theoretical models, but predicted values are generally too high and empirical corrections are used. Scott and Radom [15a], in a very extensive study of organic and inorganic compounds, showed that the calculated values can be corrected by use of method-specific Scale Factors, SF. The estimated SF value for the HF/6-31G(d) method was 0.8953, and higher level methods gave SF values closer to unity, but overall results were not necessarily

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* Corresponding author. Address: Departamento de Química Orgánica y Fisicoquímica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Casilla 233, Santiago-1, Chile. Tel.: +56 (2) 9782856; fax: +56 (2) 9782868.
E-mail address: fcastane@ciq.uchile.cl (F. Castañeda).

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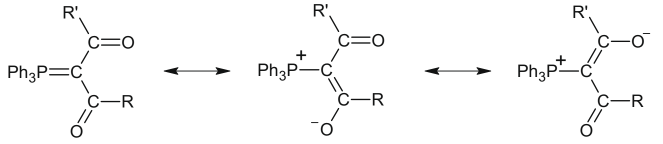
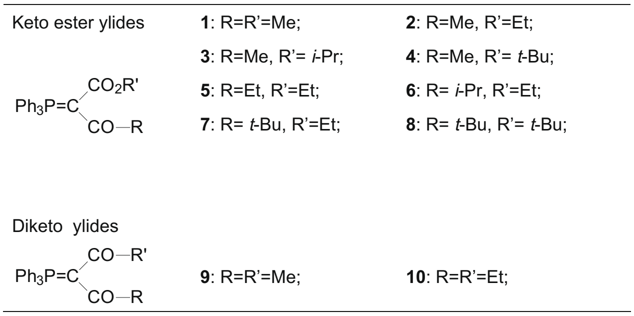


Scheme 1. Conformation of *syn–anti* diketo or keto ester ylides, R and R′ = alkyl, alkoxy.

better than from this simple method [15b]. However, the SF value for HF/6-31G(d), as applied to triphenylphosphonium diester ylides, gave frequencies which were too high and a value of SF = 0.866 gave reasonable results for a variety of diester and cyano ylides [16]. The literature SF = 0.9945 for the pure DFT functional BLYP/6-31G(d) was used for several triphenylphosphonium ylides of known conformation, and this SF correction could be neglected within the limitations of experimental error, although we apply it to all the results from this method. Silverstein et al. [17] noted that experimental wave numbers can generally be observed to within 10 cm^{-1}, which sets a limit to the required accuracy of a prediction.

For a number of triphenylphosphonium diester and cyano ylides estimated acyl stretching frequencies from both the DFT functional BLYP/6-31G(d), and HF/6-31G(d) with our revised SF value, agreed reasonably well with experiment [16]. However, for *syn–anti* conformers with a small (Me or Et) *syn* ester group and a large (isoPr or *t*-Bu) *anti* ester group the BLYP/6-31G(d) method gave good results for the *anti* acyl group, but frequencies for the *syn* acyl group were too low by 33–61 cm^{-1} and well outside the limits of experimental error. Corresponding values from the hybrid DFT functional B3LYP/6-31G(d), with the literature SF = 0.9614, were slightly higher than experimental values for the larger ester groups and lower for the smaller ester groups, but here the SF value cannot be neglected. The HF/6-31G(d) method with the revised SF gave reasonable fits with the large ester groups, but this SF value was estimated from data on all the diester ylides [16].

The ability of a large alkoxy group in an *anti* ester residue to affect the predicted acyl stretching frequency of the small *syn* ester group indicates that there are interactions between these groups, despite their separation by the ylidic carbon, and they are probably not treated fully by BLYP/6-31G(d). We cannot transpose these groups in diesters where the smaller ester group is always *syn* [16], and were unable to isolate diester ylides with two bulky alkoxy groups, but it is possible to make these structural changes in keto ester ylides where earlier evidence from X-ray crystallography and NMR spectroscopy showed that the keto acyl group is always *syn* and the ester group is *anti*, regardless of the size of its alkoxy residue [6,7,18]. Experimental and predicted stretching frequencies had been compared for some keto esters with a small (methyl) syn-keto group and a variable *anti* ester group (Me, Et, isoPr, *t*-Bu) [16]. For this series of ylides (Chart 1) the DFT functional BLYP/6-31G(d) with the near unity SF gave good fits, unlike the situation with some diesters, and the HF/6-31G(d) method, with our revised SF = 0.866, gave good fits for the ester acyl group, but predicted values for the keto acyl group were too high [16]. The ylidic *syn–anti* dimethyl ketone [8a] was also examined and here fits were good with BLYP/6-31G(d), but both HF/6-31G(d) and B3LYP/6-31G(d) gave predicted values for the keto groups which were too high, as discussed later. Examination of a series of keto ester ylides with different keto alkyl groups and various sized ester groups (Chart 1), should complement earlier results [16] on interactions between *syn* and *anti* groups and extend the earlier limited examination of diketo ylides which had indicated that the SF value for HF/6-31G(d), estimated for the ester groups, is inappropriate for keto groups. Behaviors of keto and ester groups may differ because of the geometries of the alkyl and alkoxy groups and the marked electronic delocalization in the latter.



Compounds **1-4**, and **9** have conformations from X-ray crystallography [9b, 18].

Chart 1. General structures for keto ester and diketo ylides.

Conformations of most of the ylidic diesters and the methyl keto ester ylides examined to date have been determined by X-ray crystallography [9b,10,11b,18] and bond lengths and angles are similar to those from the HF/6-31G(d) optimizations.

Observation of π-shielding [6,19] in the ^{1}H NMR signals of a terminal methyl hydrogen by a phenyl group indicates that an alkoxy group in an *anti* ester residue is oriented towards phosphorus. Results of this test have been consistent with evidence from X-ray crystallography and we used it in establishing conformations of ester groups [11,20], but the sensitivity is low for *t*-butoxy groups where the shielding effect is spread over nine methyl hydrogens.

2. Experimental

2.1. Materials

Some of the ylides examined in this work (Chart 1) were known compounds described earlier [7,8a,b], and most of the keto esters with small ester groups and various keto alkyl groups were prepared by standard methods.

The new keto ester ylides, **5–8**, were prepared by classical transylidation [20] of a alkoxycarbonylmethylenetriphenylphosphorane, $Ph_3P = CH–CO_2R'$, with acyl chlorides, R–COCl, in dry benzene, at 25° C, under an inert atmosphere. The reaction is an acid–base interaction with a second equivalent of ester ylide, as described for keto ester ylides **1–4** by Castañeda et al. [7]. Elemental analyses confirmed the structures of ylides **5–8**.

Ethyl 2-triphenyl phosphoranylidene-3-oxovalerate, ***5***. Yield 92%, m.p. 124 °C, ^{1}H NMR ($CDCl_3$) δ_{ppm}: 0.66 (t, 3H, CH_3, J = 7 Hz); 1.10 (t, 3H, CH_3, J = 7.5 Hz); 2.96 (q, 2H, CO–CH_2, J = 7.5 Hz); 3.77 (q, 2H, O–CH_2, J = 7 Hz); 7.5 (m, 15H). IR (KBr): 1558, 1658 cm^{-1}.

Ethyl 2-triphenylphosphoranylidene-4-methyl-3-oxovalerate, ***6***. Yield 72%, m.p. 180–183 °C, ^{1}H NMR($CDCl_3$) δ_{ppm}: 0.63 (t, 3H, CH_3, J = 7 Hz); 1.04 (d, 6H, CH(CH_3)$_2$); 3.47 (m, 1H, O–CH); 4.03 (q, 2H, O–CH_2, J = 7 Hz); 7.45 (m, 15H). IR (KBr): 1556, 1654 cm^{-1}.

Ethyl 2-triphenylphosphoranylidene-4,4-dimethyl-3-oxovalerate, ***7***. Yield 85%, m.p. 154 °C, ^{1}H NMR ($CDCl_3$) δ_{ppm}: 0.65 (t, 3H, CH_2–CH_3, J = 7 Hz); 1.30 (s, 9H, C(CH_3)$_3$); 3.60 (q, 2H, O–CH_2, J = 7 Hz); 7.4 (m, 15H). IR (KBr): 1531, 1658 cm^{-1}.

t-Butyl 2-triphenylphosphoranylidene-4,4-dimethyl-3-oxovalerate, **8**. Yield 76%, m.p. 130–131 °C, ^{1}H NMR ($CDCl_3$) δ_{ppm}: 1.03 (s, 9H, O–C(CH_3)$_3$); 1.32 (s, 9H, CO–C(CH_3)$_3$); 7.35 (m, 15H). IR (KBr): 1577, 1661 cm^{-1}.

2.2. IR spectroscopy

Spectra were examined on Bruker IFS 56 FT or on Leitz III-G spectrometers.